

Zirconocene-catalyzed Copolymerizations of Ethylene with 5-Methyl-1,4-hexadiene as Non-conjugated Diene[†]

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Abstract : The mixtures of non-conjugated dienes, 4-methyl-1,4-hexadiene and 5-methyl-1,4-hexadiene (MHD), were successfully synthesized by the reaction of isoprene with ethylene using Fe(III)-based catalyst in toluene. The conversion was over 96 mol% on the basis of the initial amount of isoprene used. The production yield for MHD was nearly 50 mol%, the other was polyisoprene. The mixtures were successfully copolymerized with ethylene by using zirconium-based metallocenes. The products were characterized by the combinations of gas chromatography, high temperature gel permeation chromatography, ¹H NMR, ¹³C NMR, high temperature ¹H NMR, UV/Visible spectroscopy, and differential scanning calorimetry. It was found that 5-methyl-1,4-hexadiene was active enough to be incorporated into the copolymer chain but the corresponding isomeric material, 4-methyl-1,4-hexadiene, was inactive in metallocene-catalyzed copolymerizations. Specifically, in the zirconocene-catalyzed copolymerizations of ethylene with MHD, *ansa*-structure catalysts seem to be more efficient than non-bridged type zirconocene. The degree of incorporation of MHD in the resulting copolymers was able to be controlled by the amount of non-conjugated dienes used initially.

Keywords : zirconocene, copolymerization, functional poly(α -olefin), non-conjugated diene.

Introduction

Recent advances in metallocene-catalyzed polymerizations of α -olefins have opened a new era in the polymer industry since the finding of a remarkable efficiency of partially hydrolyzed trialkylaluminum as a cocatalyst.¹ Further interests in metallocene-catalyzed polymerization arise from the production of stereoregular polymers of α -olefins,²⁻⁴ vinyls,⁵ and cycloolefins.⁶ More recent improvements in a synthetic challenge are the successful syntheses of polyolefin elastomer using a sandwich type of metallocene catalyst and of linear low density polyethylene by Insite[®] Technology.^{7,8} The excellent reviews for other dinuclear metallocene compounds as catalysts for preparation of polyolefins have been reported.^{9,10} These advances may contribute to expansion of the application fields of the final products. In spite of these successful syntheses of polymeric materials, there are still

much unsolved problems to expand their potential applications because of poor interaction with other polymers in polymer blends leading to phase separation.¹¹ To expand the limited end uses, metallocene-based poly(α -olefin) graft copolymer has been synthesized by a combination of free-radical polymerization.¹² One of the known methodologies to modify the physical properties of polymers is the incorporation of functional groups into the polymer chain leading to the increase of compatibility with other materials by chemical reactions or physical interaction such as hydrogen bonding.

Non-conjugated dienes seem to be incorporated into the polymer chain resulting in the production of functionalized polyolefins. For instance, copolymerizations of propylene with 1,5-hexadiene or 1,7-octadiene have been performed using syndiospecific isopropylidene(cyclopentadienyl)(9-fluorenyl) zirconium dichloride as metallocene catalyst leading to the production of cycloolefin polymers.¹³ Up to date, no synthetic methodology for polyolefins carrying vinyl pendant group has been reported. Presumably, these polyolefins can be applied as an intermediate for further post-reaction leading to the productions of the other functionalized polyolefins.

[†]Dedicated to Dr. Un Young Kim on the occasion of his retirement.

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Specifically, to improve the flame retardant property of the formed polyolefins, halogen atom can be incorporated into the pendant vinyl units. Incorporation of polar group into the pendant vinyl groups may produce a useful compatibilizer to be used in the polymer blending system.

In this communication, we report the results for copolymerizations of ethylene with the mixture of 4-methyl-1,4-hexadiene (4-MHD) and 5-methyl-1,4-hexadiene (5-MHD) leading to the production of poly(ethylene-*co*-MHD), which can be readily modified by further post-reaction.

Experimental

Materials. Ethylene (DaeLim Industrial Co., reagent grade) was used after passing through columns containing molecular sieve (type 3Å and 4Å) equipped with oxygen trap before delivering into the main reactor. Toluene (Oriental Chem. Co., reagent grade) was purified by following the procedures described in the literature.¹³ The mixture of 4-methyl-1,4-hexadiene and 5-methyl-1,4-hexadiene was synthesized by the reaction of isoprene (Aldrich Chem. Co., 98% pure) with ethylene (DaeLim Industrial Co.) in toluene at 80°C by following the procedures described in the literature.¹⁴ *racemic*-1,1'-Ethylene bis(indenyl)zirconium dichloride (*rac*-Et(Ind)₂ZrCl₂; Strem Chem. Co., 99%+pure), *racemic*-1,1'-dimethylsilyl bis(indenyl)zirconium dichloride (*rac*-DMSi(Ind)₂ZrCl₂), bis(1-indenyl)zirconium dichloride ((Ind)₂ZrCl₂), bis(cyclopentadienyl)zirconium (Cp₂ZrCl₂), and bis(pentamethylcyclopentadienyl)zirconium (Cp'₂ZrCl₂) were all purchased from the Strem Chemical Company and used as metallocene catalysts without further purification. Modified methylaluminoxane (MAO; Aldrich Chem. Co., 10 wt% in toluene) was purchased and used as co-catalyst without further purification.

Copolymerization of 5-methyl-1,4-hexadiene with Ethylene. The purified toluene was first delivered into a 1 L autoclave glass reactor equipped with a stirrer after complete evacuation using a high vacuum technique as shown in Figure 1. The mixture of 4-methyl-1,4-hexadiene (4-MHD) and

5-methyl-1,4-hexadiene (5-MHD) (50/50, mol/mol) dissolved in toluene was then delivered into the reactor through the cylinder (a) shown in Figure 1. Total volume of the reactants inside the reactor kept a 200 mL, followed by increasing the temperature of the reactor to 40°C. Next, the reactants was saturated with ethylene under 2 bar pressure for 30 min, followed by addition of a required amount of catalyst and co-catalyst ([Al]/[Zr] = 1,000~5,000) under argon gas pressure. All the copolymerizations of ethylene with MHD were carried out under constant ethylene pressure at 40°C for both 30 and 100 min, followed by termination with degassed methanol. The polymerization rate was monitored by the amount of consumption of ethylene passed through a mass flowmeter (Bronkhorst model). The product was washed several times with methanol and dried in vacuum oven at 40°C for at least 48 h.

Characterization. The molecular weights and the molecular weight distributions were determined by size exclusion chromatographic analysis using a Waters 150C ALC/GPC system equipped with two Styragel[®] columns (HT-4 and HT-5) performed at a flow rate of 0.3 mL/min in *o*-dichlorobenzene at 140°C after calibration using the standard polystyrene samples (Polymer Lab.). ¹H NMR spectroscopic analysis of MHD and the polymer samples was performed using a Varian Gemini-200 spectrometer with CDCl₃ and a Varian UNITY plus-600 (600 MHz) with deuterated 1,1',2,2'-tetrachloroethane (CD₂Cl₄) as solvent. The mole ratio of 4-methyl-1,4-hexadiene (4-MHD) to 5-methyl-1,4-hexadiene (5-MHD) produced from the reaction of isoprene with ethylene was determined by gas chromatographic analysis using Young Lin GC 600D equipped with a Petrocol DH capillary column (Supelco; 100 m×0.25 mm; 0.25 μm film coated) and FID detector performed at a flow rate of 4 mL/min using He gas as carrier with keeping the temperature at 250°C in both the injector and the detector, and 200°C in column. Differential scanning calorimetric analysis of the products was carried out using a Perkin Elmer DSC-7 instrument. The thermograms were obtained in the range from room temperature to 200°C by scanning with 10°C/min of the heating rate under the inert N₂ gas.

Results and Discussion

Synthesis of Methyl-1,4-hexadiene (MHD). A facile synthetic route for methyl-1,4-hexadiene as non-conjugated diene, which may be copolymerized with α-olefins using a Z-N catalytic system resulting in the production of polyolefins carrying a pendant vinyl group, has been well known for a long time.¹⁴ For instance, as shown in Scheme I, from the reaction of isoprene with ethylene, i.e., R₁ represents methyl group (-CH₃), R₂ and R₃ are hydrogens, the molar ratio for the production yield of 4-methyl-1,4-hexadiene (4-MHD) and 5-methyl-1,4-hexadiene (5-MHD) was reported to be 5.7/4.3. In this experiment, the conversion of isoprene used

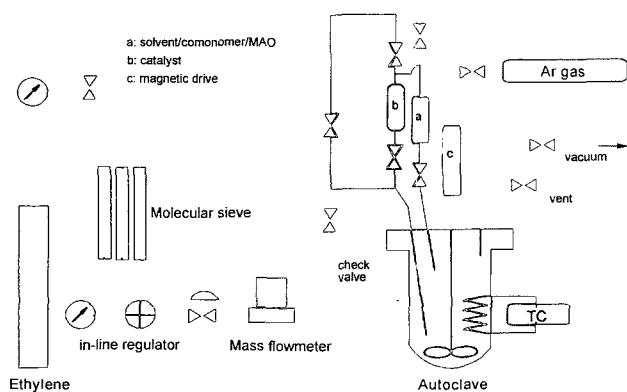
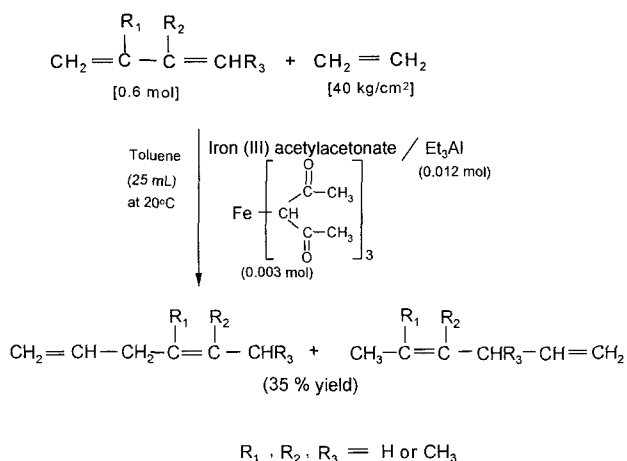
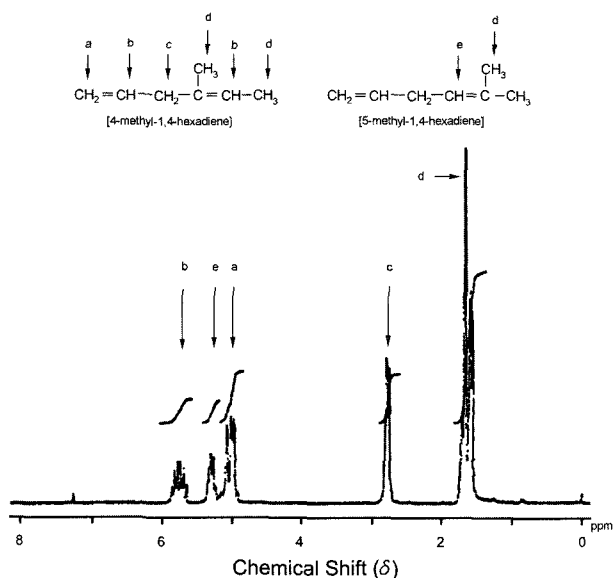


Figure 1. Schematic diagram of experimental setup.



Scheme I


 Figure 2. Typical ^1H NMR spectrum of the mixture of 4-MHD and 5-MHD.

initially was over 95 mol%. The production yield for MHD was about 50 mol% on the basis of the incipient amount of isoprene used, the other was a by-product, polyisoprene obtained from thermal polymerization of isoprene at 80°C . The ratio of 4-MHD to 5-MHD produced was usually 5.7/4.3 based on ^1H NMR and GC analysis. The typical ^1H NMR spectrum of the mixture of 4-MHD and 5-MHD is shown in Figure 2. The boiling points of 4-MHD and 5-MHD were $88\text{--}89$ and 92.8°C , respectively. Practically, it is difficult to obtain pure 5-MHD only to be copolymerizable with α -olefins through any purification methods. The chemical shifts at $\delta = 5.2$ ppm and near 1.7 ppm are assigned as the protons on the methine and the methyl groups of the mixture of the non-conjugated dienes. Based on these results, a quantitative amount of each diene can be deter-

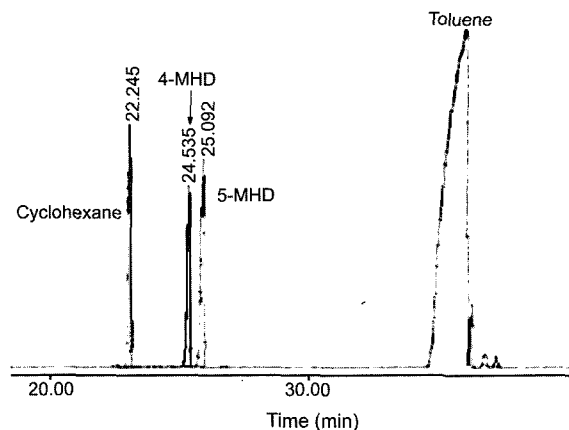
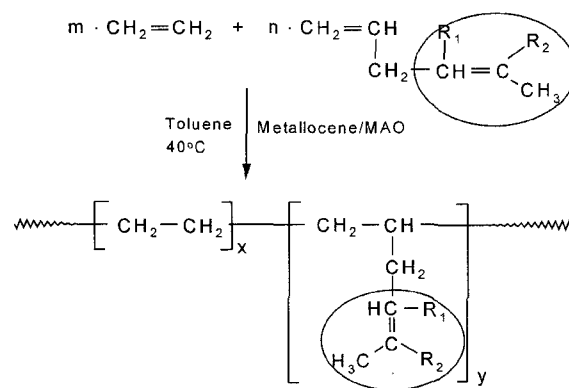


Figure 3. Gas chromatographs of the mixture of 4-MHD and 5-MHD.

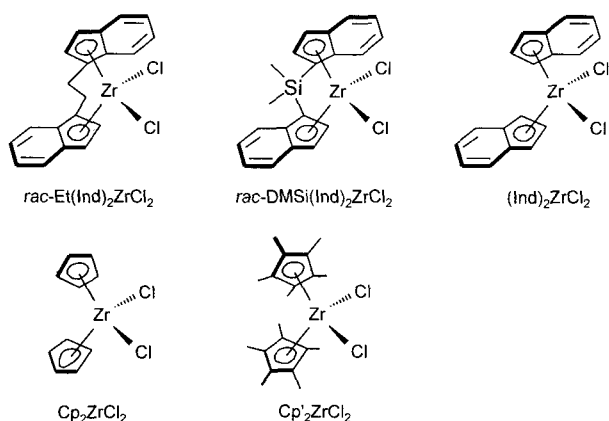


Scheme II

mined. Gas chromatographic (GC) analysis also provided the information on each fraction for 4-MHD and 5-MHD. The typical chromatograph of the mixture of dienes is shown in Figure 3. From these results, the production yields for the 5-MHD in the crude product could be determined (4-MHD/5-MHD = 4.3/5.7).

Copolymerization of Ethylene with Non-conjugated Dienes. As mentioned in the previous section, homogeneous Z-N catalyzed (including metallocene) copolymerization of ethylene with non-conjugated dienes may produce a useful polyolefins carrying vinyl groups leading to production of functional polymers through further post-reactions, as shown in Scheme II.

To synthesize effectively polyolefin including vinyl pendant group, a proper selection of homogeneous Z-N catalyst is a key factor. In this copolymerization, we first investigated the reactivities of zirconocenes, e.g., *racemic*-ethylenebis(1-indenyl) zirconium dichloride (*rac*-Et(Ind) $_2$ ZrCl $_2$), *racemic*-dimethylsilylbis(1-indenyl)zirconium dichloride (*rac*-DMSi(Ind) $_2$ ZrCl $_2$), bis(1-indenyl)zirconium dichloride ((Ind) $_2$ ZrCl $_2$), bis(cyclopentadienyl)zirconium dichloride (Cp $_2$ ZrCl $_2$), or bis(pentamethylcyclopentadienyl)zirconium dichloride (Cp' $_2$ ZrCl $_2$)



Scheme III

shown in Scheme III. The reaction conditions and the results are summarized in Table I. Specifically, the mixture of 4-MHD and 5-MHD (4/5, mol/mol) in the copolymerizations was used as the co-monomer because of their separation difficulty. From these results, *rac*-Et(Ind)₂ZrCl₂-catalyzed copolymerization of ethylene with MHD was found to produce relatively a reasonable molecular weight of copolymer including the MHD units. It has been well known that *ansa*-structure zirconocenes are more effective than the corresponding non-bridged zirconocene or half-sandwich type zirconocenes or titanocenes in the synthesis of stereoregular polymers from α -olefin polymerizations.² Practically, non-bridged sandwich type of catalysts such as (Ind)₂ZrCl₂, Cp₂ZrCl₂, or Cp'₂ZrCl₂ seem to be inactive for copolymerization of olefin with higher alkyl chain monomer as shown in Table I. Interestingly, Cp'₂ZrCl₂-catalyzed copolymerization produced not copolymer but homopolyethylene with relatively high yield. This phenomenon may arise from higher reactivity due to the electron-donating methyl groups on the cyclopentadienyl ring compared with the correspondingly unsubstituted Cp₂ZrCl₂, however, its reactivity seems to be too enough to activate the non-conjugated dienes or higher alkyl chain olefins. The indenyl group seems to be less

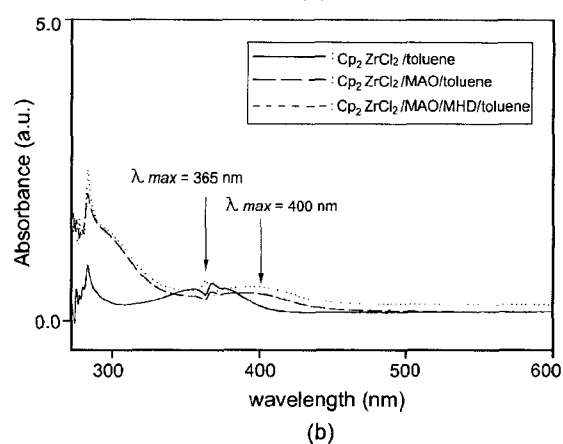
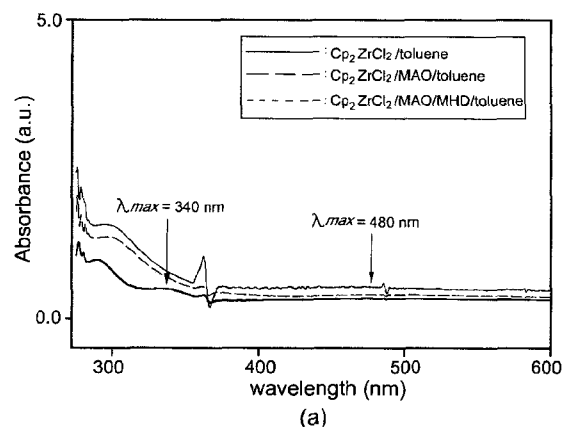


Figure 4. Comparison of UV/Vis spectra of Cp₂ZrCl₂ (a) and Cp'₂ZrCl₂ (b) catalytic system.

effective than the Cp' group to stabilize even though the former contains π -electrons for stabilization of 'cation-like' metal center considering a charge transition between Cp-based HOMO and Zr-based LUMO.¹⁵ The UV/Visible spectrum of Cp₂ZrCl₂ retains the absorption maximum at $\lambda_{max} = 340$ nm and its corresponding MAO complex exhibit weak absorption intensity at $\lambda_{max} = 480$ nm (a bathochromic shift) as shown in Figure 4(a). The electronic spectral

Table I. The Reaction Conditions and the Results for Synthesis of Poly(Ethylene -*co*- MHD) Using Zirconocene/MAO Catalytic System in Toluene for 30 min

Catalyst	[Al]/[Zr] (mol/mol)	MHD ^a (mmol)	Yield (g)	MHD Contents ^b (mol%)	T_m (°C)	\bar{M}_n ^c	PDI ^d
Cp ₂ ZrCl ₂	5,000/1	25	0.8	0	128	12,000	2.5
Cp' ₂ ZrCl ₂	5,000/1	25	4.6	0	141	84,000	2.8
(Ind) ₂ ZrCl ₂	5,000/1	25	×	×	×	-	-
<i>rac</i> -Et(Ind) ₂ ZrCl ₂	5,000/1	25	9.0	2.2	113	21,000	4.3
<i>rac</i> -DMSi(Ind) ₂ ZrCl ₂	5,000/1	17	3.6	1.4	117	10,000	9.5

^aThe incipient amount of the MHD mixture used in copolymerization.

^bThe mole % of incorporated 5-MHD in the copolymer chain determined by ¹H NMR.

^cThe number average molecular weight of copolymer obtained by high temperature GPC.

^dThe molecular weight distribution obtained by high temperature GPC.

change of $\text{Cp}'_2\text{ZrCl}_2$ catalytic system exhibits relatively less bathochromic shift (365 nm \rightarrow 400 nm) with adding MAO. In most metallocene catalytic systems, this phenomenon usually informs that the latter seems to be more active than the former in ethylene polymerization. The result listed in Table I exhibits that the reactivity of the latter is higher than that of the former, in which the production yields were 0.8 and 4.6 gram, respectively.

In comparison of the catalytic activities of *ansa*-structure zirconocenes, *rac*-Et(Ind) $_2$ ZrCl $_2$ is more efficient than *rac*-DMSi(Ind) $_2$ ZrCl $_2$ due to less steric hindrance considering the cone angle between the ligands. Thus, *rac*-Et(Ind) $_2$ ZrCl $_2$ was selected as the proper catalyst in this copolymerization. To optimize the copolymerization conditions, copolymerizations were performed at a constant amount of comonomer with the MAO concentration. The reaction conditions and the characterization results are shown in Table II.

The molecular weight of copolymer rather decreased with increasing the MAO concentration while the incorporated amount of MHD into copolymer was not affected as shown in Table II and Figure 5 representing size exclusion chromatograms of the resulting copolymers. From these results, it can be deduced that the high concentration of MAO can make not only both ethylene and a non-conjugated diene difficult to be diffused into the active site sterically but also α - or β -hydride elimination of the growing chain easy leading to the production of a low molecular weight of copolymer. However, it is not completely excluded that the initial concentration of comonomer may affect to the degree of incorporation of comonomer in this copolymerization although thermodynamic effect on the degree of incorporation of non-conjugated diene was not determined. Figure 6 is the typical ^1H NMR spectrum of poly(ethylene-*co*-MHD), entry 3, in Table II. The chemical shift at $\delta = 5.2$ ppm is assigned to the methine proton on the pendant vinyl group. Surprisingly, only incorporation of 5-methyl-1,4-hexadiene (5-MHD) into the copolymer was observed on the basis of ^1H NMR analysis. Furthermore, GC analysis of the crude product solution after removal of copolymer and MAO by filtration informed that a proper amount of consumption of

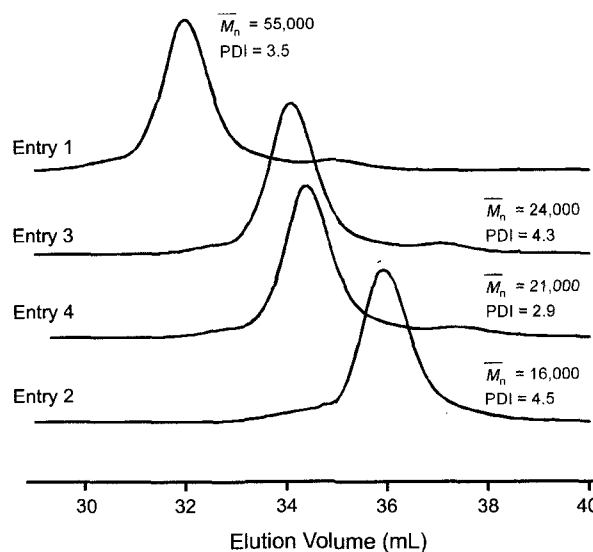


Figure 5. Size exclusion chromatograms of copolymers shown in Table II.

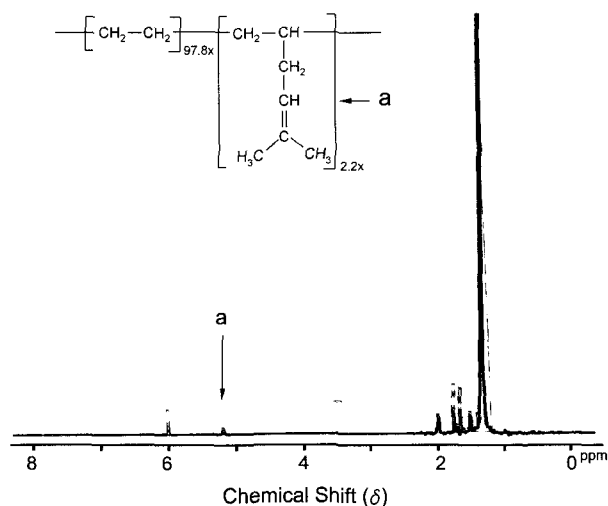


Figure 6. Typical ^1H NMR spectrum of poly(ethylene-*co*-MHD), entry 3, in Table II.

Table II. The Reaction Conditions and the Results for Characterization of Poly(Ethylene-*co*-MHD) Synthesized by *rac*-Et(Ind) $_2$ ZrCl $_2$ /MAO Catalytic System in Toluene at 40 °C for 30 min

Catalyst	[Al]/[Zr] (mol/mol)	MHD ^a (mmol)	Yield (g)	MHD Contents ^b (mol%)	T_m (°C)	\bar{M}_n ^c	PDI ^d
1	2,000/1	25	1.0	2.4	110	55,000	3.5
2	3,000/1	25	3.0	2.6	111	16,000	4.9
3	5,000/1	25	9.0	2.2	113	21,000	4.3
4	7,000/1	25	1.5	2.6	108	24,000	2.9

^aThe feed monomer used in copolymerization initially.

^bThe mole percent of incorporated MHD into copolymer.

^cThe number average molecular weight of poly(ethylene-*co*-MHD) using high temperature GPC.

5-MHD was observed but the concentration of 4-MHD was unchanged in comparison with the initial concentration of the mixture of 4-MHD and 5-MHD. One possible suggestion is that the methyl group at the 4-position may provide more electron donating effect the π -electron of the vinyl group on the 4,5-position and less steric hindrance effect leading to the easy formation of complex with the 'cation-like' metal center compared to the 1-vinyl unit. This may not only limit a coordination of the 1-vinyl group to the active center resulting in no chance for incorporation of 4-MHD but also decrease the reaction rate of the other monomers. Thus, it is concluded that the reactivity ratio of 4-MHD to ethylene seems to be negligible for zirconocene-catalyzed copolymerization with ethylene.

Conclusions

We synthesized successfully the mixture of 4-methyl-1,4-hexadiene (4-MHD) and 5-methyl-1,4-hexadiene (5-MHD) from the reaction of ethylene with isoprene using Fe(III)-based catalyst. The production yields were about 50 mol% which was determined by GC analysis on the basis of the incipient amount of isoprene used. Among zirconocene catalysts, *ansa*-structure zirconocenes are more effective than sandwich type of non-bridged zirconocenes for this copolymerization system.

Functionalized polyolefins were successfully synthesized by zirconocene-catalyzed copolymerizations of ethylene with MHD. 5-MHD was found to be only incorporated into the polymer chains in zirconocene-catalyzed copolymerizations of ethylene with the mixture of 4-MHD and 5-MHD. A proper choice of catalyst and the MAO concentration as co-catalyst should be required for getting an optimum property such as molecular weight of poly(ethylene-co-5-MHD). The MAO concentration did not affect to the incorporation of MHD in this copolymerization system.

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References

- (1) H. Sinn and W. Kaminsky, *Adv. Organomet. Chem.*, **18**, 99 (1980).
- (2) H. H. Brintzinger, D. Fischer, R. Mulhaupt, B. Rieger, and R. M. Waymouth, *Angew. Chem. Int. Ed. Engl.*, **34**, 1143 (1995).
- (3) W. Kaminsky, *Macromol. Chem. Phys.*, **197**, 3907 (1996).
- (4) (a) R. W. Barnhart and G. C. Bazan, *J. Am. Chem. Soc.*, **120**, 1082 (1998); (b) L. Resconi, F. Piemontesi, I. Camurati, O. Scedmeijer, I. E. Nifantev, P. V. Ivchenko, and L. G. Kuzmina, *J. Am. Chem. Soc.*, **120**, 2308 (1998).
- (5) (a) N. Ishihara, M. Kuramoto, and M. Uoi, *Macromolecules*, **21**, 3356 (1988); (b) D. J. Duncalf, H. J. Wade, C. Waterson, P. J. Derrick, D. M. Haddleton, and A. McCamley, *Macromolecules*, **26**, 6399 (1996); (c) Y. Li, D. G. Ward, S. S. Reddy, and S. Collins, *Macromolecules*, **30**, 1875 (1997); (d) A. Zambelli, L. Oliva, and C. Pellecchia, *Macromolecules*, **22**, 2129 (1989); (e) J. Kim, K. H. Kim, Y. H. Jin, H. Ryu, S. Kwak, K. U. Kim, S. S. Hwang, W. H. Jo, and J. Y. Jho, *Korea Polym. J.*, **8**, 44 (2000).
- (6) (a) S. Collins and W. M. Kelly, *Macromolecules*, **25**, 233 (1995); (b) W. M. Kelly, S. Wang, and S. Collins, *Macromolecules*, **30**, 3151 (1997); (c) M. Arndt and W. Kaminsky, *Macromol. Symp.*, **95**, 167 (1995).
- (7) R. Kravchenko, A. Masood, R. M. Waymouth, and C. L. Myers, *J. Am. Chem. Soc.*, **120**, 2039 (1998).
- (8) (a) P. J. Shapiro, W. D. Cotter, W. P. Schaefer, J. A. Labinger, and J. E. Bercaw, *J. Am. Chem. Soc.*, **114**, 4623 (1994); (b) D. Schwank, *Modern Plastics Int.*, Aug., 33 (1993).
- (9) (a) D. H. Lee and S. K. Noh, *Korea Polym. J.*, **9**, 71 (2001); (b) D. H. Lee, H. Lee, W. S. Kim, K. E. Min, L. S. Park, K. H. Seo, I. K. Kang, S. K. Noh, C. K. Song, S. S. Woo, and H. J. Kim, *Korea Polym. J.*, **8**, 231 (2000).
- (10) J. Kim, K. H. Kim, S. Kwak, and K. U. Kim, *Polym. Sci. Technol. (Korea)*, **9**, 17 (1998).
- (11) (a) T. C. Chung and D. Rhubright, *J. Polym. Sci.; Part A; Polym. Chem.*, **33**, 829 (1996); (b) T. C. Chung, *Macromolecules*, **21**, 865 (1988).
- (12) U. M. Stehling, E. E. Malmstrom, R. M. Waymouth, and C. J. Hawker, *Macromolecules*, **31**, 4396 (1998).
- (13) N. Naga, T. Shiono, and T. Ikeda, *Macromolecules*, **32**, 1348 (1999).
- (14) (a) J. G. Bryson, *U. S. Pat.* 3,904,704 (1975); (b) G. Hata, *J. Am. Chem. Soc.*, **64**, 3903 (1964).
- (15) (a) D. Coevoet, H. Cramail, and A. Deffieux, *Macromol. Chem. Phys.*, **199**, 1451 (1998); (b) J.-N. Pedeutour, D. Coevoet, H. Cramail, and A. Deffieux, *Macromol. Chem. Phys.*, **200**, 1215 (1999).